

Carbon dioxide emission in Italy: Shallow crustal sources or subduction related fluid recycling?

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Anomalous 'non-volcanic' CO₂ release in central and southern Italy has been highlighted by ten years of detailed investigations on Earth degassing processes. Two regional degassing structures are located in the Tyrrhenian sector where more than 200 emissions of CO₂ are located and has been recently included in the first web based catalogue of degassing sites (<http://googas.ov.ingv.it>). The total amount of CO₂ released by the two structures were evaluated to be $> 2 \times 10^{11}$ mol a⁻¹ ($> 10\%$ of the estimated global volcanic CO₂ emission). The anomalous flux of CO₂ suddenly disappears in the Apennine in correspondence of a narrow band where most of the Italian seismicity concentrates. Here, at depth, the gas accumulates in crustal traps generating CO₂ overpressurised reservoirs. These overpressured structures are, in our opinion, one of the main cause of Apennine earthquake activation processes. The results of these investigations suggested that Earth degassing in Italy may have an active primary role in the geodynamics of the region. What is the origin of gas? The large extension of the degassing structures and petrologic data suggested that the main source of gas is a mantle metasomatised by the fluids produced in the subducted slabs. However, has been also hypothesised the presence of localised crustal source of the gas. This matter will be discussed on the base of unpublished isotopic data of the main gas emissions.

Electrochemical study of FeS corrosion in acid solutions in the presence of benzothiazolic compounds

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Iron monosulfide (FeS) exposed to acidic solutions containing oxidants can dissolve oxidatively [1, 2]. This corrosion releases toxic elements (heavy metals and arsenic) present in the FeS matrix. However, this corrosion may be altered by interaction with organic molecules. 2-(cyclohexylaminomercapto)-benzothiazole (CMB) and 2-mercaptobenzothiazole (MBT) are known to inhibit corrosion of steel [3]. The present study investigated the effect of these molecules on FeS.

The behaviour of synthetic FeS in acid solutions at 25°C in the presence and the absence of CMB or MBT was investigated using electrochemical measurements and microscopic analysis. The corrosion currents (i_{corr}) were obtained from Tafel polarization plots [3]. The polarization resistance in absence and presence of inhibitors (R_p^0 and R_p , respectively) were determined from electrochemical impedance spectroscopy. It was observed that both CMB and MBT reduce the oxidative (anodic) dissolution of FeS. For example, in 0.1 mol L⁻¹ HCl i_{corr} decreases from 342 $\mu\text{A cm}^{-2}$ (in the absence of inhibitors) to 65 $\mu\text{A cm}^{-2}$ ([CMB] = $5 \cdot 10^{-4}$ mol L⁻¹) and to 95.8 $\mu\text{A cm}^{-2}$ ([MBT] = $5 \cdot 10^{-4}$ mol L⁻¹). Instead R_p increases from 33.4 $\Omega \text{ cm}^2$ in the absence of inhibitors to 175.4 and to 119.3 $\Omega \text{ cm}^2$ in the presence of CMB and MBT, respectively. These results indicate that CMB is a more efficient inhibitor than MBT. It was also found that the FeS surface coverage [$\theta = 1 - (R_p^0/R_p)$] increases when inhibitor concentration augments from $2 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ mol L⁻¹. This is in good agreement with microscopic images that indicate the formation of a protective film on the FeS surfaces corroded in presence of inhibitors.

All these findings suggest that FeS corrosion can be substantially reduced by the formation of organic layers that may modify the electronic properties of FeS/water interface.

[1] Chirita *et al.* (2008) *J. Colloid Interface Sci.* **321**(1) 84-95.

[2] Chirita & Descostes (2006) *J. Colloid Interface Sci.* **294**(2) 376-384. [3] Samide & Bibicu (2008) *Surf. Interface Anal.* **40**(5) 944-952.